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Unraveling Li-Ion Solvation Dynamics in Ether-Based Electrolytes via High-Throughput Molecular Dynamics Simulations and Machine Learning

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Abstract: Lithium-ion batteries (LIBs) are now widely used as energy storage systems in portable electronic devices and electric vehicles. The Li-ion solvation dynamics in electrolytes significantly influence the overall performance of LIBs. In this work, we performed high-throughput molecular dynamics smilations on thousands of ether-based electrolytes screened from a vast molecular database containing over 110 million organic molecules. Machine learning models combined with Shapley additive explanation analysis reveal that the presence of bulky alkyl groups reduce the solvent dipole moment, while enhancing the coordination ability of lithium ions with anions. Additionally, the introduction of ether-type groups (-O-) in the rings of cyclic ether molecules negatively affects the solvent dipole moment but positively influences the Li-anion coordination number. In contrast, ether-type groups (-O-) introduced in linear chains correlate positively with solvent dipole moment while negatively with the Li-anion coordination number. This work provides insights into the relation between molecular structure and Li-ion solvation dynamics in electrolyte solutions.

Key words: Li-Ion solvation, machine learning, high-throughput molecular dynamics simulations, electrolyte structure-property relation.

1. Introduction

Lithium-ion batteries (LIBs) have been revolutionized energy storage technology due to their high energy density, lightweight design, and rechargeability. They have dominated the portable-electronic market and showed great promise in large-scale application, such as electric vehicles and smart grids [1-3]. Liquid electrolytes, acting as the 'blood' of LIBs, consist of solvents and lithium salts. Salt ion pairs dissociate in the solvents, with lithium ions surrounded by solvents and/or anions to form lithium-ion solvation sheath. The interactions between cations and solvents [4], cations and anions [5], and anions and solvents [6] determine the solvation environments, leading to the formation of different ion-solvent complexes, such as solvent-separated ion pairs (SSIPs), contact-ion pairs (CIPs) and nano-aggregates (AGGs). These solvation structures significantly influence the overall performance of LIBs [7-11]. For instance, many studies report that LIBs employing weakly-solvated electrolytes, characterized by AGG-dominated solvation structures, outperform those with SSIP-dominated electrolytes under low-temperature and high-voltage conditions [8,9,11,12]. Moreover, AGG-dominated solvation structures promote the formation of inorganic-rich solid electrolyte interphase (SEI), which enhance the stability of lithium-metal batteries [13-15].

Theoretical work has also been conducted to understand elucidate how Li-ion solvation structures affect electrolyte properties

[16-21]. Grossman et. al [16] performed classical molecular dynamics (CMD) simulations to study Li-ion solvation dynamics in various types of electrolyte systems. Rai et. al [17] investigated how Li-ion solvation structures, modulated by salt concentration, impact ion transport in the ethylene carbonate–$LiPF_6$ system. Hamada et al [18]. performed first-principles molecular dynamics simulations on lithium-ion solvation in mixtures of triglyme and lithium bis (trifluoromethylsulfonyl) amide (LiTFSA). It is worth to note that most studies have focused on Li-ion solvation dynamics in a limited number of solvents, which may be insufficient to fully understand the impact of diverse solvation structures on electrolyte properties. In this study, we combined high-throughput MD simulations with machine learning techniques to systematically study the structure-property relationships in ether electrolyte systems.

Recent advances in computational technologies have enabled the integration of machine learning models with high-throughput computation to accelerate the discovery of optimal materials for lithium-ion/metal batteries [22-27]. Compared to traditional experimental trialand-error approaches, computational screening significantly reduces the time required for the material design and experimental validation. For instance, Troyer et al. identified 18 promising solid state electrolytes from 32 million materials using machine learning model combined with high-throughput computation [22]. Their top candidates, $Na_xLi_{3-x}YCl_6$ ($0 \leq x \leq 3$) series, were subsequently synthesized and experimentally validated, demonstrating their high performance. Ma et. al developed a machine-learning workflow to screen fluoroether-based electrolytes for high-stability lithium metal batteries [27].

In this study, approximately 3000 ether molecules were initially selected from the Pub-Chem database, which contains over 100 million organic molecules. Sequent high-throughput MD simulations were carried out to calculate dipole moments and Li-anion/-solvent coordination numbers. Machine learning analysis indicates that alkyl groups correlate negatively with the solvent dipole moment, yet positively correlate with the Li-anion coordination number. Moreover, we find that stronger Li-anion coordination strength corresponds to a lower percentage of SSIPs and a higher percentage of AGGs in the lithium-ion solvation structures. These findings provide valuable insights into the effects of Li-ion solvation structures on electrolyte properties.

2. Molecular dynamics simulations

Molecular dynamics simulations were performed using GROMACS 2023 package [28,29]. Lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) was used as lithium salt. In the high-throughput MD simulations, each electrolyte system contains 600 solvent molecules and the number of LiTFSI molecules was set to mimic 1 mol/L LiTFSI electrolytes. The force field parameters for solvents and ions were derived from the general AMBER force field (GAFF) [30,31], where the atomic charges were generated from restrained fitting on the electrostatic potential (RESP) [32,33] calculated at HF/aug-cc-pVTZ, using Gaussian 16.A.03 software [34]. The atomic charges of ions were scaled down by a factor of 0.7 to account for the neglect of electronic polarization in CMD simulations. After being minimized by the steepest-descent algorithm, the systems were further equilibrated in the NPT ensemble using a thermal annealing approach with a total time of 5 ns. The temperature of systems was initially raised from 0 K to 400 K in a period of 0.5 ns. After being maintained at 400 K for 2 ns, the systems were cooled down to 298 K within 0.5 ns and equilibrated at 298 K for an additional 2 ns. Subsequently, a 20 ns NPT simulation was conducted to sample the structures for data analysis. The temperature was controlled by the V-rescale thermostat with a damping time constant of 0.3 ps, and the pressure was maintained at 1 bar using the C-rescale barostat with a time constant of 2 ps. The cutoffs for the short-range electrostatic and van der Waals interactions were set to 1.2 nm. The calculations of dipole moments, radial density functions (RDFs) and coordination numbers (CNs) of Li-anion/solvent pairs were performed using the post-processing tools implemented in GROMACS software package.

The residence time τ of the $TFSI^-$ anion measures the kinetics of the formation/dissociation of Li^+s solvation structures, which is computed using the Li-anion residence correlation function given by

$$C(t) = \frac{\langle H(t)H(0)\rangle}{\langle H(0)H(0)\rangle},$$

where H denotes the Heaviside function. If the $TFSI^-$ anion reside in the first solvation sheath of Li^+ ion, $H(t) = 1$, otherwise $H(t) = 0$. The cutoff distance defining the first solvation shell of Li^+ is taken as the Li-$TFSI^-$ distance corresponding to the first minimum of the radial distribution function (RDF). The mean residence time τ of the $TFSI^-$ anion was obtained by fitting the exponential function to the residence correlation function.

3. Machine learning methods

The extended connectivity circular fingerprints (ECFPs) [35] implemented in the chemoinformatics toolkit RDKit package [36] was used as molecular descriptor, with each molecule represented as a 2048-dimensional vector. The 2048-dimensional vector of ECFP fingerprints has been reduced to 1353- and 935-dimensional vectors for ring and chain ether molecules, as many fragments do not exist in the ether molecules considered in the present work. Machine learning models, including support vector regression (SVR), random forest (RF), Gaussian process regression (GPR), gradient boosting regression (GBR) and multi-layer perceptron regression (MLP), implemented in scikit-learn package [37] were used to predict the solvent dipole moment and Li-anion coordination number, respectively. Five-fold cross-validation was used for model selection. The mean absolute error (MAE) was employed as the criterion to examine the accuracy of the fitting models. The machine learning model was combined with Shapley additive explanation (SHAP) [38] method to unravel the correlation between the solvent molecular subgroups and targets (i.e., dipole moment, coordination number).

4. Results and discussion

The ether molecules were screened from the public database PubChem, which contains over 110 million organic molecules. To this end, the screening started by considering compounds that only contain carbon, hydrogen and oxygen elements. To this end, the screening started by considering compounds that only contain carbon, hydrogen, and oxygen elements. The compounds with carbonyl groups, hydroxyl groups, and/or unsaturated carbon-carbon bonds were excluded during the screening. The large organic molecules with more than 8 carbon atoms were excluded, as larger ethers often suffer from high viscosity, leading to reduced ionic